Inorganica Chimica Acta, *72* (1983) 181–186

Reactions of Tin(IV) Chloride with Organosilyl Compounds

NARAYAN S. HOSMANE*

Department of Chemistry, Southern Methodist University, Dallas, Tex. 75275, U.S.A.

STEPHEN CRADOCK and E. A. V. EBSWORTH

Department of Chemistry, Edinburgh University, West Mains Road, Edinburgh, EH9 3JJ, U.K.

Received December 2, 1982

The reaction between $SnCl_4$ *and* $R_{3-n}SiH_{n+1}$ *(n = 0–2) have been investigated [R =* CH_3*,* $CH=CH_2$*,* $CH_2-CH=CH_2$*,* $C\equiv CH$*,* $C\equiv CCF_3$*,* C_5H_5*,* C_6H_5*, or* $Si(CH_3)_3$*]; the reaction with silacyclopent-3-ene was also investigated. All the reactions led to monochlorination at silicon without breaking the Si–C and/or Si–Si bonds except in some allylsilanes, and spectroscopic parameters for the new compounds* $\overline{CH_2-CH=CH-CH_2Si}HCl$*,* $CH\equiv CSiH_2Cl$*,* $CF_3C\equiv CSiH_2Cl$*,* $(CH_3)_3SiSiH_2Cl$*, and* $(CH_3)_3SiSiHCl_2$*, all prepared by this route, are reported. For the disilanes,* ^{29}Si *and* ^{13}C *chemical shifts were measured by heteronuclear double resonance.*

Introduction

We have already described [1] a study of the influences of tin(IV) chloride as a chlorinating agent for inorganic compounds containing the SiH_3 group. In this paper we describe the reaction between the same reagent and a variety of organosilanes containing SiH– and Si–Si bonds with a view to establishing the range of organosilanes that can be chlorinated by tin(IV) chloride without breaking Si–Si and Si–C bonds.

Experimental

Compounds were handled in standard vacuum-systems fitted with greased taps or teflon valves; all the reactions were carried out in pyrex-glass ampoules of 30 ml capacity fitted with teflon valves, involatile substances were manipulated in evacuable glove-bags or boxes under an atmosphere of dry N_2.

Spectra were obtained by means of the following instruments: infrared, Perkin-Elmer 225 (500–200 cm^{-1}) or 457; Raman, Cary 83 (aγ ion laser source, 488 nm); Mass, AEI MS 902; NMR HA 100 (100 MHz for ^1H) whose probe has been double-tuned to accept a second radio-frequency [2]. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. All the known compounds among the products were identified by comparing their infrared and ^1H NMR spectra with those of the authentic samples.

Reaction of the Tin(IV) Chloride

With Methylsilane

Methylsilane (1.02 mmol) was allowed to warm to room temperature with $SnCl_4$ (1.43 mmol) A thin white film began to form almost immediately; the reaction appeared complete after 4 hr. The volatile products consisted of HCl (1.03 mmol), CH_3SiH_2Cl (0.87 mmol) and CH_3SiHCl_2 (0.15 mmol); a white involatile residue of $SnCl_2$ (1.05 mmol) remained.

With Dimethylsilane

Dimethylsilane (1.00 mmol) was allowed to warm to room temperature with $SnCl_4$ (1.16 mmol). A white solid began to form almost at once and the reaction appeared complete after 20 minutes. The volatile products consisted of HCl (1.00 mmol) and $(CH_3)_2SiHCl$ (1.00 mmol); a white involatile residue of $SnCl_2$ (1.00 mmol) remained.

With Trimethylsilane

Trimethylsilane (1.00 mmol) was allowed to warm to room temperature with $SnCl_4$ (1.40 mmol). A thin white film of solid began to form almost at once; the reaction appeared complete after 3 hr. The volatile products consisted of HCl (1.00 mmol) and Me_3SiCl (1.00 mmol); $SnCl_4$ (0.31 mmol) was

---

*Author to whom correspondence should be addressed.

0020-1693/83/$3.00

TABLE I. Raman and Infrared Spectra of $ClSiH_2C{\equiv}CH$.

Liquid[a]		Vapor[a]	
Raman frequency (cm^{-1})	Raman polarization ratio	Infrared frequency (cm^{-1})	Possible assignments
3310 vvw	p?	3313.8 s	νCH
		2247.3 w	?
2220 vvs	p	2219.1 vs	νSiH (asym)
		2215 s	νSiH (sym)
		2204.4 s	?
2060 vs	p	2061.8 s	$\nu C{\equiv}C$
		1362 m	2 × 692 (overtone)
950 ± 1 s, broad	dp?	955 s	δSiH_2
		934 ± 1 m	?
870 w, broad	dp?	874.6 vs	δSiH_2
		815 vw	δSiH_2
810 vvw, broad	dp?		
735 m, broad	dp?	729.8 vw	C_2H_2 impurity
710 w, broad	dp?	692 s	ρSiH_2
670 ± 2 w	p?	663 w	νSiC
620 ± 5 vw, broad	dp?	628? m	δCCH (asym)
		615 m	δCCH (sym)
535 vvs	p	548 m	νSiCl
325 w, broad	p?	322 w	SiCC bend (asym)
222 s	dp?		SiCC bend (sym)
132 vs	dp?		ClSiC bend

[a] Where s = strong, m = medium, w = weak, v = very, p = polarised and dp = depolarised.

recovered, and a residue of $SnCl_2$ (1.00 mmol) remained.

With Methylchlorosilane

Methylchlorosilane (0.37 mmol) was allowed to warm to room temperature with $SnCl_4$ (0.39 mmol). A white solid began to form slowly. After 3 days, the products were found to consist of HCl (0.21 mmol) and CH_3SiHCl_2 (0.23 mmol); CH_3SiH_2Cl (0.13 mmol) and $SnCl_4$ (0.15 mmol) were recovered, and a residue of $SnCl_2$ remained. In a separate experiment, CH_3SiH_2Cl (0.80 mmol) was allowed to stand over $SnCl_2$ (2.0 mmol); all the CH_3SiH_2Cl (0.80 mmol) was recovered unchanged.

With Vinylsilane

Vinylsilane (1.00 mmol) and $SnCl_4$ (1.50 mmol) were allowed to warm to room temperature; white solid began to form at once and the reaction appeared complete after 18 hours. The volatile products consisted of HCl (1.11 mmol), SiH_3Cl (0.11 mmol), vinylchlorosilane (0.67 mmol), and vinyldichlorosilane (0.21 mmol); unreacted $SnCl_4$ (0.25 mmol) was recovered. In a second experiment, vinylsilane (2.00 mmol) and $SnCl_4$ (1.50 mmol) gave HCl (1.50 mmol), $ClSiH_2CHCH_2$ (1.50 mmol) and vinylsilane (0.50 mmol).

With Allylsilane

Allylsilane (1.00 mmol) and $SnCl_4$ (1.2 mmol) were allowed to warm together to room temperature. A white solid began to form at once; the reaction appeared complete after 2 hours. The volatile products consisted of HCl (0.12 mmol), SiH_3Cl (0.60 mmol), SiH_2Cl_2 (0.40 mmol) and $ClCH_2$-$CHCH_2$ (0.80 mmol); a white involatile residue of $SnCl_2$ remained.

With Phenylsilane

Phenylsilane (1.00 mmol) and $SnCl_4$ (1.50 mmol) were allowed to warm together to room temperature. A thin white film began to form almost at once; the reaction appeared complete after 15 minutes. The volatile products were found to consist of HCl (0.92 mmol), SiH_3Cl (0.04 mmol), SiH_2Cl_2 (0.02 mmol) and $PhSiH_2Cl$ (0.91) mmol; $SnCl_4$ contaminated with a little benzene (0.5 mmol in all) was also recovered, and a residue of involatile $SnCl_2$ remained.

TABLE II. Raman and Infrared Spectra of $ClSiH_2CCCF_3$.

Liquid[a]		Vapor[a]	
Raman frequency (cm^{-1})	Raman polarization ratio	Infrared frequency (cm^{-1})	Possible assignments
2238 vs	p	2226 s	νSiH (asym)
		2221.5 s	νSiH (sym) + νC≡C
1265 vvw, br	dp	1252.6 vs	
1225 vvw	dp	1223 s	νC–F
1172 vw, br	dp	1180 vvs	
948 s	dp	947 s	δSiH_2
880 s	p	–	?
865 m	dp	868 vs	δSiH_2
742 m	p	760 vvw	δSiH_2
731 m	dp	726 vvw	ρSiH_2
702 w	p	698 vvw	νSiC
620 m	dp	610 m	δCF_3
558 vs	p	564 s	νSiCl
462 m	dp	467 vvw	δCF_3
378 m	dp?	372 m	δCF_3
305 vs	p	302 vvw	CCC bend?
243 ± 1 vvs	dp	–	SiCC bend?
151 vvs	dp?	–	ClSiC bend?

[a] Where s = strong, m = medium, w = weak, br = broad, v = very, p = polarised, and dp = depolarised.

With Cyclopentadienylsilane

Cyclopentadienylsilane (0.50 mmol) was allowed to warm with $SnCl_4$ (0.70 mmol) to room temperature. A grey-white solid formed immediately, and this reaction was complete in 3 minutes. The volatile products were found to consist of HCl (0.07 mmol), SiH_3Cl (0.43 mmol) and SiH_2Cl_2 (0.07 mmol). Attempts to record the infrared spectrum of the solid residue were unsuccessful.

With Silacyclopent-3-ene

Silacyclopent-3-ene (1.00 mmol) and $SnCl_4$ (1.03 mmol) were allowed to warm together to room temperature. A white solid began to form at once and reaction appeared complete after 30 minutes. The volatile products were found to consist of HCl (volatile at –78 °C) and 1-chlorosilacyclopent-3-ene [collected in a trap at –78 °C, 1.00 mmol. Exact mass M.W. for $^{35}Cl^{28}SiC_4H_7$, $^{37}Cl^{28}SiC_4H_7$, Calc. 118.000555, 119.997605; Found: 118.000813, 119.997921. ^1H NMR spectrum, Si*H* triplet (J = 2.8 Hz) at δ4.67 ppm, multiplets δ1.9 and δ4.8–6 ppm. Raman peaks at 3054m, 2918sp, 2195vs, 1612m, 1405m, 1285sh, 1211mp, 918s, 763m, 718vs, 640s, 530wsp, 235m, 197s. IR peaks at 2960sh, 2850sh, 2175s, 1108m, 857s, 755m, 643m, 528m. *Anal.* Calcd. for C_4H_7ClSi: C, 40.51; H, 5.91; Cl, 29.95; Si. 23.63. Found: C, 40.54; H, 5.82; Cl, 29.89; Si, 23.66].

With Silylacetylene

Silylacetylene (1.00 mmol) was allowed to warm to room temperature with $SnCl_4$ (1.50 mmol). White solid began to form at once; the reaction apppeared complete after 18 hours. The volatile products consisted of HCl (volatile at –130 °C, 0.50 mmol), SiH_3Cl (volatile at –120 °C, 0.07 mmol), unreacted silylacetylene (volatile at –120 °C, 0.43 mmol), and chlorosilylacetylene [volatile at –78 °C but involatile at –120 °C, 0.50 mmol. M(Dumas), found 91.3; calc. 90.5. M(exact mass), $^{35}Cl^{28}SiC_2H_3$, $^{37}Cl^{28}SiC_2H_3$, found, 89.968993, 91.966740; calc. 89.969256, 91.966306. v.p. at 0 °C, 16.2 cm Hg; b.p. (extrap.) = 321 K. δ(SiH)) = 4.79, δ(CH) = 2.48 ppm. (Me_4Si solvent and internal standard); $^4J(HH)$ = 1.0 Hz. Vibrational spectra and assignments are summarized in Table I. *Anal.* calcd for C_2H_3ClSi: C, 26.52; H, 3.31; Cl, 39.23; Si, 30.94. Found: C, 26.43; H, 3.42; Cl, 39.19; Si, 31.02].

With 1-Silyl-3,3,3-trifluoropropyne

1-silyl-3,3,3-trifluoropropyne (1.0 mmol) was allowed to warm to room temperature with $SnCl_4$ (0.95 mmol); white solid began to form at once and

TABLE III. Raman and Infrared Spectra of Me_3SiSiH_2Cl.

Liquid[a]		Vapor[a]	
Raman frequency (cm^{-1})	Raman polarization ratio	Infrared frequency (cm^{-1})	Possible assignments
2970 s	dp	2958 ± 1 m	
2910 s	p	2900 w	νCH
		2869 vvw	
2140 ± 2 vs	p	2138 ± 1 s	νSiH
1410 w,br	dp	1410 w,br	δCH_3 (asym)
		1325 ± 1 vvw	
1265 w	p?	1262 m	δCH_3 (sym)
1252 w	dp		
940 m,br	dp	945 ± 2 w,br	δSiH_2
870sh			ρCH_3
845 vw,br	dp	845 s,br	
805 ± 2 vw	p?	802 ± 2 vs	δSiH_2
755 vw	dp	743 w	$\rho\ SiH_2$?
702 s	dp	698 w	νSiC
630 vs	p	620 w	νSiC
525 ± 2 m,br	dp?	530 ± 1 m	νSiCl
478 m	p	490 vvw	?
418 vvs	p	405 vvw	νSi–Si
223 vs	dp		δC_3Si
180 s	p?		
150s	dp?		ClSiSi bend?

[a] Where s = strong, m = medium, w = weak, sh = shoulder, br = broad, p = polarised and dp = depolarised.

the reaction appeared complete after 18 hours. The volatile products consisted of HCl (collected in a −196 °C trap, 0.95 mmol), unreacted SiH_3CCCF_3 (collected in a −120 °C trap, 0.05 mmol), and 1-chlorosilyl-3,3,3-trifluoropropyne [volatile at −78 °C but involatile at −96 °C, 0.95 mmol. M(Dumas), found, 158; required 158.5. M(exact mass mass spectrum), 157.956151, 159.953273. $C_3H_2ClF_3Si$ requires 157.956638 (^{35}Cl), 159.953688 (^{37}Cl). $^{\delta}$(Me_4Si solvent and standard), 4.88; $^{\delta}$F, −53.42 (low frequency of CCl_3F solvent and standard) $^1J(^{29}SiH)$ = 265, $^5J(HF)$ = 1.3 Hz. Vibrational frequencies and assignments are summarised in Table II. *Anal.* Calcd for $C_3H_2ClF_3Si$: C, 22.71; H, 1.26; Cl, 22.40; F, 35.96; Si, 17.67. Found: C, 22.80; H, 1.30; Cl, 22.38; F, 35.89; Si, 17.70].

With 1,1,1-Trimethyldisilane

1,1,1-trimethyldisilane (1.0 mmol) and $SnCl_4$ (0.96 mmol, 0.258 g) were condensed in a 20-ml reaction ampoule and allowed to warm to room temperature. A thin white film on the inner walls of the reaction ampoule began to form almost immediately, and the reaction was complete in 5 minutes. Trap-to-trap distillation of the volatile products gave HCl (0.96 mmol) volatile at −120 °C, unreacted Me_3SiSiH_3 (0.04 mmol) volatile at −78 °C, and Me_3SiSiH_2Cl [0.96 mmol, collected in a −78 °C trap. M(Dumas), found 139; required 138.5. M (exact mass), 138.008335, 140.006094. $C_3H_{11}ClSi_2$ requires 138.008782 (^{35}Cl), 140.005832 (^{37}Cl). ^1H NMR spectrum (C_6H_6 solvent and standard, Si*H* [$^1J(H^{29}Si)$ = 204 Hz; $^2J(HSi^{29}Si)$ = 11 Hz] singlet at $^{\delta}$4.66 ppm, *H*CSi singlet at δ 0.02 ppm; $^1J(H^{13}C)$ = 120 Hz, $^2J(HC^{29}Si)$ = 6.6 Hz, $^3J(HCSi^{29}Si)$ = 3.8 Hz. $^{\delta 29}Si$ (relative to Me_4Si; negative to low frequency $Me_3^{28}Si^{29}SiH_2Cl$ = −30.75 ppm, Me_3^{29}-$Si^{28}SiH_2Cl$ = −15.7 ppm. $^{\delta 13}C$ = −5.52 ppm. Vibrational frequencies and assignments are summarized in Table III. *Anal.* calcd. for $C_3H_{11}ClSi2$: C, 26.0; H, 7.9; Cl, 25.6; Si, 40.4. Found: C, 26.1; H, 7.8; Cl, 25.5; Si, 40.5.]

TABLE IV. Raman and Infrared Spectra of $Me_3SiSiHCl_2$.

Liquid[a]		Vapour[a]	
Raman frequency (cm^{-1})	Raman polarization ratio	Infrared frequency (cm^{-1})	Possible assignments
2965 m	dp	2968 ± 2 w	
2902 s	p	2910 ± 2 vw	νCH
		2850 vvw	
2170 vs	p	2171 ± 2 m	νSiH
1415 ± 5 vw,br	dp	1405 vvw	δCH_3 (asym)
1250 ± 5 vw,br	dp	1258 m	δCH_3 (sym)
1055 vvw	dp?		?
915 vvw,br	dp?		
		865 sh	δSiH
850 ± 5 vw,br	dp?	845 m	
775 w	dp	778 s	ρCH_3
738 m	dp	734 m	ρSiH
702 w	dp	704 sh	νSiC
625 vs	p	622 vw	νSiC
542 sh	dp?	558 s	νSiCl (asym)
525 m	p?	532 m	νSiCl(sym)
392 vvs	p	395 vvw	νSi–Si
258 m	dp?	–	?
215 s	dp?	–	δC_3Si
178 m	dp?	–	
152 s	dp?	–	ClSiSi bend
095? vw	p?	–	ClSiCl bend?

[a] Where s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very, p = polarised and dp = depolarised.

With 1,1,1-Trimethyl-2-chlorodisilane

Me_3SiSiH_2Cl (1.0 mmol) was allowed to warm to room temperature with $SnCl_4$ (1.03 mmol, 0.27 g); white solid began to form slowly and the reaction appeared complete after 24 hours. The volatile products consisted of HCl (collected in a trap at −196 °C, 1.0 mmol), and $Me_3SiSiHCl_2$ [volatile at −45 °C but involatile at −78 °C, 1.0 mmol. M(Dumas), found, 173; required 173. M(exact mass), 171.969783, 173.966723, 175.964341. $C_3H_{10}Cl_2Si_2$ requires 171.969810 (^{35}Cl, ^{35}Cl), 173.966854 (^{35}Cl, ^{37}Cl), 175.963910 (^{37}Cl, ^{37}Cl). ^1H NMR spectrum (C_6H_6 solvent and standard), Si*H* [$^1J(H^{29}Si)$ = 235 Hz; $^2J(HSi^{29}Si)$ = 18.8 Hz] singlet at δ5.58 ppm, *H*CSi [$^2J(HC^{29}Si$ = 7.0 Hz; $^2J(HCSi^{29}Si)$ = 5.0 Hz; $^1J(H^{13}C)$ = 121 Hz] singlet at δ–0.01 ppm. $\delta^{29}Si$ (relative to Me_4Si; negative to low frequency) $Me_3^{28}Si^{29}SiHCl_2$ = +12.08 ppm, $Me_3^{29}Si^{28}SiHCl_2$ = −6.54. $\delta^{13}C$ = −3.78 ppm. Vibrational frequencies and assignments are summarized in Table IV. *Anal.* calcd for $C_3H_{10}Cl_2Si_2$: C, 20.8; H, 5.78; Cl, 41.0; Si, 32.4. Found: C, 20.8; H, 5.75; Cl, 40.9; Si, 32.5].

Discussion

Our results suggest that tin(IV) chloride is a convenient reagent for chlorinating SiH-groups in organosilanes other than some allylsilanes; cyclopentadienylsilane can be regarded as an allylsilane. As with inorganic molecules containing SiH_3-groups, reaction to introduce a single chlorosubstituent at a silicon atom is much faster than to introduce a second. We made no quantitative studies of rates of reaction; however, it is clear that reaction between $SnCl_4$ and $Me_{3-n}SiH_{n+1}$ (n = 0–2) is fastest when n = 1. It seems likely that the rate of reaction depends on a combination of steric and electronic factors. This would explain why the rate increases with increasing methyl substitution at silicon until steric factors become important. This is consistent with a mechanism involving electrophilic attack at silicon. The observation that the Sn(II) chloride produced forms an adherent film on the ampoule wall suggests that reaction occurs predominantly in a liquid film of Sn(IV) chloride. The product $SnCl_2$ + HCl might be formed by decomposition of an initial product

$HSnCl_3$, but we have obtained no evidence for the formation of this species.

The cleavage of the Si–C bonds in allylsilane and cyclopentadienylsilane may involve initial formation of organotin(IV) derivatives:

$$RSiH_3 + SnCl_4 \rightarrow [RSnCl_3] + SiH_3Cl$$

We were unable to identify such a derivative in either case. The isolation of allyl chloride in 80% yield from reaction of allylsilane and tin(IV) chloride would then imply the ready decomposition.

$$[RSnCl_3] \rightarrow RCl + SnCl_2.$$

The reaction with silylcyclopentadiene yielded no chlorocyclopentadiene; the possibility of polymerization complicates the problem in this case.

It is interesting that significant quantities of SiH_2Cl_2 were found in the reactions of allylsilane and cyclopentadienylsilane. These could not have been formed indirectly by reaction of initially-formed SiH_3Cl with unreacted $SnCl_4$, as this reaction is very slow. It may be that the postulated intermediate $[RSnCl_3]$ is a better chlorinating agent than $SnCl_4$. We intend to investigate this point using alkyl substituted tin(IV) chloride.

References

1 S. Cradock, E. A. V. Ebsworth and N. S. Hosmane, *J. Chem. Soc. Dalton Trans., 16/17,* 1624 (1975).
2 D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.,* 2518 (1972).